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THE ETCHING BEHAVIOR OF URANIUM DIOXIDE-TUNGSTEN COMPOSITES

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THE ETCHING BEHAVIOR OF URANIUM DIOXIDE-TUNGSTEN COMPOSITES

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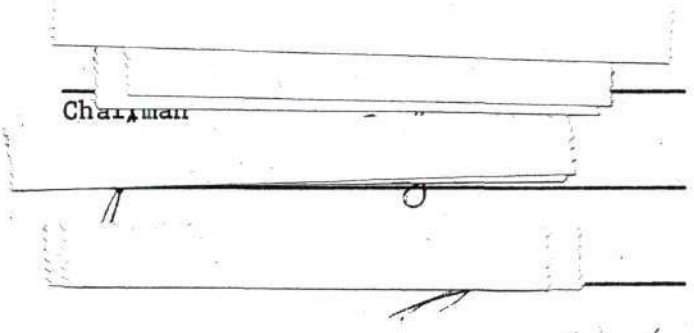

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SUMMARY

Chemical and electrochemical etching of UO_2-W composites formed by unidirectional solidification was studied. Emphasis was placed on alteration of the composite structure to form optimum emitting pin arrays by exposure of the W pins above the UO_2 matrix, shaping of the W pins, and removal of the W pins. Favorable results in exposure and shaping of the W pins were obtained using an etchant of chromic acid, nitric acid, acetic acid, and hydrofluoric acid with slight variations in the relative proportions to produce the desired pin geometry. Removal of the W pins was produced by exposure to a mixture of potassium ferricyanide and sodium hydroxide.

CHAPTER I

INTRODUCTION

A new form of cermet has been recently developed which is composed of a refractory oxide and a metal and which combines the advantages of both materials. Eutectic (coupled, unidirectional) solidification of refractory oxide-metal mixtures has led to this novel class of composites. In these composites the metal grows in the form of well ordered fibers less than one μ in diameter imbedded in an oxide-matrix (e.g. W in UO_2 or in ZrO_2).[1,2]

The growth of a composite from a refractory oxide and a refractory metal possessing dissimilar chemical and physical properties results in a material with unique anisotropic properties and which offers a class of high temperature materials of great potential. The very stable nature of the oxides and the excellent bonding between metal and metal oxide, combined with uniformly spaced micron-size metallic fibers or platelets, provide materials which exhibit unique mechanical properties, and hence, are of potential interest for many structural applications. The prospects of "softening" the brittle nature of the oxides using small oriented metal precipitates is most attractive. The very anisotropic nature of the various oxide-metal combinations offers novel electrical and magnetic properties. The different chemical nature of the oxide and metal permits the selective etching of the matrix to expose the ordered array of over one million metallic fibers

per square centimeter. Such structures have enormous potential for electron emission under both field emission and thermionic activation. The practical application of this class of composites as emitters is realistic because the unidirectional solidification growth scheme readily produces samples of usable emitter size.

Current mathematical descriptions of the electron emission from point sources may be used to calculate optimum emitting array geometries for the different emitting modes. An individual field emitter is normally shaped in the form of a needle with a tip of small radius. When a voltage is applied, the local electric field near the tip is very high and field emission occurs from the tip. This constitutes the well-known type of cold electron emitter, whose maximum steady state current per needle can be 10^{-4} amps.

However, when there is an array of such needles as is found in the refractory oxide-metal composites, there is generally a very strong interference effect, which reduces the local electric field at each tip. This field can be reduced by factors of 10, 100, 1000, etc., depending on the parameters of the array. To overcome this huge effect, it is possible to optimize (for maximum total current) the geometry (fiber height, tip radius, lattice size) in terms of the voltage and interelectrode spacing.[3]

The alteration of pin array geometry in these composites may be attained by variations in the growth mechanism, chemical etching, or mechanical approaches. Chemical and electrolytic etching techniques currently used to shape emitter tips for the field emission microscope may be employed to shape the metal pins of the composite.

Cline[4] has studied field emission from nickel-tungsten composites grown by eutectic directional solidification. The composite structure consisted of an array of parallel 2μ wires. A multineedle field emission cathode was made by selectively etching and pointing the tungsten filament tips. From this cold cathode, the voltage characteristics of a simple diode were studied and found to follow the Fowler-Nordheim field emission equation. A field emission microscope was constructed using a multineedle cathode to observe the emission distribution; it was concluded that the current was not uniformly distributed over the filaments.

Another alteration to composite structures was made by Desorbo and Cline[5] in which a metal membrane with submicron size pores was produced from a metal-metal composite. Porous metal wafers and thin films were produced by selectively etching the rod phase of the directionally solidified eutectics and by a two-state replication process, respectively. The half micron diameter holes were uniform in size and distribution. The flow properties of these porous membranes were tested using liquids of different viscosities and were found to be in agreement with Poisseuille's law.

In this investigation, the etching of uranium dioxide-tungsten composites to obtain structures suitable for electron emission was studied. First, the processes for selectively removing the UO_2 matrix with little or no attack on the W pins, shaping of the exposed W fibers for optimum emitting performance, and removal of the W fibers with little or no attack on the UO_2 matrix will be described; then, the results of these alterations to the structure will be discussed.

CHAPTER II

SURVEY OF LITERATURE

Unidirectional solidification of a uranium dioxide and tungsten melt by internal centrifugal zone growth results in the formation of well-ordered arrangements of tungsten fibers in the uranium dioxide matrix. The tungsten fibers are quite well ordered with the spacing between fibers ranging from 3 to 6 μm and diameters between 0.25 and 1 μm.[3,6]

In order that unidirectionally solidified UO_2-W composites may be used efficiently as electron emitters, their structure can be altered to (1) expose the W pins above the UO_2 matrix, (2) shape the W pins into optimum emitting structures, and (3) remove a section of the W pins so that the oxide matrix acts as a resistor in series with each fiber. Since this type of composite structure is relatively new, only limited literature is available on the selective treatment of UO_2 and W together. Most often information is available on pure UO_2 or pure W.

An individual field emitter normally is shaped in the form of a needle with a tip of small radius. In order to achieve this configuration from the composite structure, it is necessary to expose the W fibers above the UO_2 matrix and shape them into points. Acid mixtures for the selective etching of the UO_2 matrix for exposure of the W fibers have been derived from etchants for the thinning of UO_2

for transmission electron microscopy with modifications made to reduce the chemical attack on the W fibers. With other modifications these etchants will attack the W at a slower rate than the UO_2, resulting in the exposure and shaping of the W fibers in a one step process.

Much work has been done on the shaping of W wires for emitter tips in the field ion microscope. These techniques include chemical and electrochemical methods which may be possible means of shaping the W fibers in the UO_2-W composites.

Complete or partial removal of tungsten from the composite structure would allow its use as a filter or as a resistance in series with the W pins. Methods for the removal of tungsten include reaction with a mixture of an oxidant and an alkali hydroxide, molten salt baths, and electrolysis.

Due to the lack of literature of UO_2-W composites, this survey is divided into etchants for UO_2 and etchants for W. Information gathered from these separate areas was employed in selecting the etch compositions to be studied.

Uranium Dioxide

Prior to 1940 little was known about UO_2. Its primary use was as a colorant in glazes and glassware. Following the discovery of atomic energy, there was a great increase of interest in UO_2 until today it is the most widely used uranium compound in the nuclear power reactor field.[7]

The high electrical resistivity of UO_2[7] which at room temperature

ranges from 3 X 10^{+4} to nearly 10^{+6} ohms cm has made it useful as a non-conducting matrix for tungsten pins in field emission applications and thermionic emitters. However, this high resistance made polishing and etching samples of UO_2 more difficult than a material with high conductivity. When samples of UO_2 were ground and polished by hand, there was a high tendency for the material to slip strain. This was the direct cause of the appearance on the surfaces of samples, after etching, of numerous scratches originating from previous polishing. An ideal solution to the problem should be offered by electrolytic polishing, which, by reducing the preparation of the sample to simple grinding, eliminated to a great extent the cause of slip straining undergone by the material. Unfortunately, electrolytic polishing of uranium oxides was possible only when the material was of a high density (90 to 95 percent of theoretical density).[8]

For this reason, chemical etching techniques were generally used on UO_2. They had the advantages of reducing the effect of straining, operational simplicity, reproducibility of results, time saving, and optimum etching conditions.[8] Also, chemical etching was not effected by such factors as: dimensions of the sample, voltage and current applied, distance between anode and cathode, temperature, etc.[9]

The general procedure in chemical etching included grinding with silicon carbide of 180, 320, 400, and 600 grit before immersion in the etching bath. In some cases diamond paste polishing was also used.

An etching solution recommended by Bassi and Camona[9] contained chromic acid (30 percent), hydrofluoric acid and water in a ratio of

2:1:1. It was applied to the sample by swabbing for 2½ to 3 minutes. Results showed the sample to be perfectly free from scratches, and etch pits were almost completely absent while the pores were easily found.

A second etchant recommended by Bassi and Camona[9] was made of propionic acid, chromic acid, nitric acid, and hydrofluoric acid in ratio of 15:7½:5:2. Again, it was applied by swabbing on the sample for 2½ to 3 minutes. Results were comparable to their other etch.

Manley[10] used two different chemical-polishing techniques for the thinning of UO_2 samples to electron transparency for use in the transmission electron microscope. The most suitable chemical polish was based on a solution devised by Bassi and Camona[9] with acetic acid instead of propionic acid and other minor compositional adjustments:

10 ml glacial acetic acid

20 ml saturated chrome trioxide solution

5 ml 40 percent hydrofluoric acid

7 ml nitric acid

The specimen was held in stainless steel tweezers and waved vigorously in the solution. The rate of solution was approximately 2 μm/minute. Examination of these specimens in the electron microscope showed surface roughening. Alteration of the relative proportions of the etch constituents produced no improvements. It was found that the roughness could be removed by immersion for 30 minutes in a weakly alkaline solution of hydrogen peroxide. However, this solution produced triangular and hexagonal etch pits.

In an attempt to improve the quality of the samples, a second

chemical polishing solution was developed:

20 ml orthophosphoric acid

10 ml glacial acetic acid

2 ml nitric acid

Used at $120^{\circ}C \pm 5^{\circ}C$ this solution gave clean electron transparent areas. However, in order to avoid the severe pitting which accompanied dissolution, it proved better to pre-thin the specimen with the first solution until the onset of optical transparency, and subsequently to polish in the third solution. The rate of attack of the third solution was of the order of 100 μm/minute. Because of the lack of etch pits and the greater frequency of success, the method of using the first and third solutions in combination was preferred.

Manley[10] reported the use of nitric or orthophosphoric acid for thinning single crystals of UO_2 unsuccessful; nitric acid preferentially attacked the grain boundaries, and orthophosphoric acid roughened the surface. Bauleke[11] attempted to use Manley's reported solution in the chemical thinning of pneumatically impacted UO_2 but it attacked the grain boundaries too rapidly and caused the sample to fall apart. Reducing the amount of nitric acid reduced the rate of grain boundary attack. The following modified Manley composition was used by Bauleke as a working mixture for chemical thinning:

10 ml glacial acetic acid

20 ml saturated chrome trioxide solution

5 ml 48 percent hydrofluoric acid

4 ml nitric acid

Removal rate of the surface was about 2 μm/minute.

Briggs[12] investigated several solutions as etchants and chemical polishers for UO_2 single crystals. A successful etchant for edge and screw dislocations was H_2O_2-H_2O-H_2SO_4 in 6:3:1 ratios. For polishing and some concomittant etching, 88 percent orthophosphoric acid was recommended.

Kanevskii, Filippov, and Timofeeva[13] studied the composition of gases produced by the interaction of UO_2 with HNO_3. Uranium dioxide was treated with HNO_3 in H_2SO_4 in an autoclave at 85°C. An analysis of the resultant gas phase indicated that the main product was NO; only 0.3 volume percent N_2O and 1.9 volume percent NO_2 were found.

In later work by the same authors[14] in which $NaNO_2$ was added to 100 ml of solution containing 50 gm H_2SO_4 per liter and 2 gm suspended UO_2, it was found that all of the UO_2 was dissolved at a mole ratio of HNO_2:UO_2 equal to 1.88. Similar experiments on a larger scale in an autoclave indicated the formation of UO_2SO_4, NO, and H_2O.

Habashi and Thurston[15] in their work on the kinetics and mechanism of the dissolution of UO_2 proposed that this was an electrochemical process similar to the corrosion of metals. UO_2 in contact with water containing oxygen acquired electrons at one part of the surface (the cathodic zone), while UO_2 gave them up at another (the anodic zone).

The cathodic reaction was represented by:

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- \qquad (1)$$

and the anodic reaction by the equation:

$$UO_2 \longrightarrow UO_2^{+2} + 2e^- \qquad (2)$$

In neutral medium like distilled water, the uranyl ion hydrolyzed as soon as liberated, to form a hydroxide:

$$UO_2^{+2} + 2H_2O \longrightarrow UO_2(OH)_2 + 2H^+ \qquad (3)$$

In the presence of acids, the hydroxide was dissolved, as follows:

$$UO_2(OH)_2 + 2H^+ \longrightarrow UO_2^{+2} + 2H_2O \qquad (4)$$

Experimental results of the solution rates of UO_2 according to the above equations indicate that at low acid concentration the rate of solution was independent of the oxygen pressure, but depended only on the acid concentration. On the other hand, at high acid concentration, the rate was independent of the acid concentration, but depended only on the oxygen pressure. The dependence on acid concentration in the first case was linear, and on oxygen pressure in the second case was approximately linear.

Tungsten

Most applications of tungsten are derived from its good conductivity of heat and electricity. After the initial use of tungsten as filaments in incandescent lamps, it has been used as electrodes for discharge tubes, electrical contacts, heating elements and thermocouples in non-oxidizing atmospheres, X-ray cathodes, and emitters in the field ion microscope.[16]

The high electrical conductivity[16] and low work function result in good electron emission and make tungsten a good candidate for cathode materials. The most advantageous shape of tungsten commercially available for use as an electron emitter is as a fine wire. Fabrication of such a fine wire using regular metallurgical techniques is quite difficult due to the extreme refractoriness of the metal. It has been found that unidirectional solidification of a melt consisting of UO_2 and 5 to 15 weight percent W formed well ordered arrangements of tungsten fibers in the uranium dioxide matrix.[6] These fibers were approximately 1 μm in diameter and produced good electron emission when properly exposed above the electrically resistant matrix.[3]

Due to the small size of these fibers, mechanical means of shaping them was not feasible; therefore, chemical and electrochemical etching techniques were used. According to Rieck[16], tungsten is very resistant to many vigorous chemicals. At room temperature it is strongly attacked only by fluorine and dissolved by a mixture of nitric and hydrofluoric acids. Aqua regia and caustic alkalies with an oxidizing agent like hydrogen peroxide or potassium ferricyanide dissolve it below 100° C and it is slowly attacked by nitric, sulfuric, and phosphoric acids.

Neugebauer and Kiss[17] studied the dissolution rates of tungsten in the presence of an alkali and an oxidant, KOH and $K_3Fe(CN)_6$. The effects on the dissolution rates of time and temperature as well as of the KOH and $K_3Fe(CN)_6$ concentrations were investigated. At low KOH concentrations and dissolution rates, the rates corresponding to different times were practically identical, but for increased initial

KOH concentration and corresponding higher dissolution rates, the tendency of the rate curves to decline with time was more pronounced. With rising temperatures the dissolution rate rose more steeply and an ultimate rate constancy was attained at the temperatures tested (35°, 50°, and 70° C). The higher the OH^- concentration (varying from 0.2 to 1.4 moles), the higher were the dissolution rates. On increasing the concentration of $K_3Fe(CN)_6$ (from 0.125 to 0.4888 mole/1) the initial portion of the rate curve grew steeper, while the constant portions appeared at gradually higher concentrations of the OH^- ion.

Stoichiometric investigations led to the following reactions:

$$W + 6K_3Fe(CN)_6 + 6KOH \longrightarrow WO_3 + 6K_4Fe(CN)_6 + 3H_2O \qquad (5)$$

$$WO_3 + 2KOH \longrightarrow K_2WO_4 + H_2O \qquad (6)$$

$$W + 6K_3Fe(CN)_6 + 8KOH \longrightarrow K_2WO_4 + 6K_4Fe(CN)_6 + 4H_2O \qquad (7)$$

Conclusions reached from these experiments[17] were that the tungsten surface was polished when the mole ratio of $K_3Fe(CN)_6$ to KOH was greater than 2.5. When the mole ratio was equal to 2.5, an etching effect occurred. At mole ratios up to $K_3Fe(CN)_6$:KOH = 2.5, the dissolution rates increased gradually, while over 2.5 they approached constancy.

Other proposed solvents for tungsten are ammoniacal cupric hydroxide[18] and an oxalic acid—hydrogen peroxide mixture,[19] but the metal dissolves readily only in a mixture of hydrofluoric and nitric acids.[20] According to Robbins,[20] a mixture containing approximately

40 percent by volume concentrated nitric acid and approximately 60 percent by volume concentrated hydrofluoric acid was the most effective solvent. When tungsten dissolved in hydrofluoric-nitric acid mixtures, it was converted to the trioxide, WO_3, indicating that the hydrogen fluoride present in the solution had no direct chemical action on the metal and, therefore, that the main reaction resulted from the presence of nitric acid or its decomposition products which is in disagreement with Rieck.[16] In his studies, Robbins used sodium nitrate—hydrofluoric acid mixtures as his etchant. The reaction mechanism was interpreted to be the reduction of the nitrate ion together with a simultaneous oxidation of the metal, according to the equations:

$$6HF \longrightarrow 3HF_2^- + 3H^+ \tag{8}$$

$$W + 3Na^+ + 3NO_3^- + 3H^+ \longrightarrow WO_3 + 3HNO_2 + 3Na^+ \tag{9}$$

$$3HF_2^- + 3Na^+ \longrightarrow 3NaHF_2 \tag{10}$$

Nitrous acid is unstable in solution, dissociating easily by loss of water and by disproportioning:

$$2HNO_2 \longrightarrow H_2O + N_2O_3 \rightleftharpoons NO_2 + NO \tag{11}$$

$$3HNO_2 \longrightarrow HNO_3 + 2NO + N_2O \tag{12}$$

It is well known that nitrous acid often appears to catalyse the reaction of a metal with nitric acid; experiments by Robbins showed that nitrogen dioxide and/or nitrous acid reacts with tungsten.

The conclusions reached from this work indicate that the tungsten surface was oxidized by nitrogen dioxide, the oxide thus produced being soluble in hydrofluoric acid, but insoluble in other mineral acids.

Another method of etching tungsten with fluorine was reported by Barnett and Miller.[21] In this process, the tungsten sample was heated to about 1000° C in an evacuated chamber (5×10^{-7} torr). Tungsten hexafluoride gas was introduced and allowed to flow for one hour during which 1 mil of the surface was removed. It was conjectured that the WF_6 reacts with the tungsten being treated to form volatile lower fluorides of tungsten.

The high chemical resistivity of tungsten to attack by acids has caused researchers to turn to more powerful methods of etching the metal. One method frequently used is an electrolytic cell in which electric energy is used to produce chemical change.[22] Tungsten can be dissolved anodically in caustic alkali solutions, if the potential exceeds 1.05V and tungstate ions are formed. Davis[23] electropolished tungsten wire at 10 volts by immersion in a 1.5 percent caustic soda solution at 20°C for two minutes; etching occurred in a 0.75 percent caustic soda solution with 10V for 15 seconds and .75V for the remaining minute and 45 seconds.

Ammonium hydroxide and ammonium sulfate were used by Farshauer[24] to polish tungsten. Immersion time was a few seconds in the aqueous basic electrolyte with a current density of 0.5 to 1.0 amp/cm^2. Ammonium sulfate increased the initial conductivity and also the efficiency of the electrolytic bath.

Leizgol'd[25] in the electrolytic etching of tungsten for the manufacture of grids for vacuum electron devices used an electrolyte consisting of 9-10 gm of caustic potash, 6-7 gm tripotassium citrate and 85 ml of water. This electrolyte permitted a closer control over the etching process and also ensured a greater uniformity of the etching.

Relatively thin structures composed of tungsten[26] are manufactured with electrolytic etching by preparing two models from copper or nickel with the desired configuration and placing a foil of the metal between the models. The assembly is immersed in an electrochemical bath which attacks the foil but not the models, e. g. NaOH, so as to remove the areas of foil exposed by the models. The perforated foil so produced can be in the form of a grid and can if desired have a grooved edge.

A general method of electrolytically etching tungsten was used by Cline[4] in a cell containing 2 gm NaOH in 100 ml H_2O with the tungsten as the anode and a stainless steel cathode. The anode was immersed for a few seconds at a potential of 20 V dc and examined in an optical microscope. This provided precise control of the tungsten filament size by electropolishing until the filaments appeared as points of light in the microscope.

Modification of the above method was developed by Weinberg[27] because electrochemical attack is a slow process due to the build up of an insulating dissolved ion layer formed around the article being worked. In an effort to increase rate of attack without increasing electrical current, ultrasonic vibrations were used to remove the

insulating ion layer. Tungsten was immersed in an electrolyte of 100 gm NaOH and 1000 ml H_2O. A stainless steel cathode was used and a voltage of 6 volts was applied. The current density was 3-6 amps per cm^2. The rate of metal removal without ultrasonic vibrations was nil for 10 minutes of etching time, but with ultrasonic vibrations removal was 0.035 inch for 10 minutes of etching time.

Latawiec and Lockwood[28] developed a method of electropolishing tungsten using a bath of from five percent to 25 percent by weight sodium hydroxide or potassium hydroxide, or mixtures thereof, and from 10 percent to 40 percent by weight sodium tartrate, potassium tartrate, sodium potassium tartrate or any mixtures thereof, with the balance of the bath being distilled water. If the concentration of either the hydroxide or the tartrate is below the indicated minimum, the wire is electrocleaned rather than electropolished; if the concentrations are greater than the indicated maxima the electropolishing process is quite slow. Bath temperatures were between 70° and $100^{\circ}F$. The electrodes were formed of stainless steel mesh. The voltage which was applied between the two electrodes was from 16 to 18.5 volts, the current through the bath was 20 to 24 amperes, and the current density was 3,000 to 4,000 amperes per square foot of surface of wire in the bath.

This process was used to make tungsten wire with a uniform diameter and high degree of luster. It was achieved by passing the wire to be cleaned at a predetermined rate of speed through an electrolytic bath which contained a predetermined concentration of selected electrolyte which reacted with (or chelated) tungsten oxide to form a

tungsten compound which was soluble in the electrolyte.

Aqueous solutions of sodium hydroxide and potassium cyanide had been commonly used as electrolytes but they left some contamination when the specimens were used for transmission electron microscopy. A new solution which was used with success was composed of potassium compounds with hydroquinone as a reducing agent. It was subsequently found that backpolishing in an aqueous solution of 20 percent potassium sulfite with an addition of 0.5 percent hydroquinone produced a clean surface, using an alternating voltage of at least 10 volts and a second electrode of gold.[29]

According to Rieck[16], tungsten is not attacked electrochemically in acids, except in oxalic and phosphoric acid solutions in which complex ions are formed. Cortes[30] devised a method in which tungsten was electrochemically polished in an acid solution composed of five volume percent sulfuric acid and 1.25 volume percent hydrofluoric acid and the remainder methanol. The sample was exposed to a current density of 30 amps/square inch and voltage of 50 to 70 volts for eight to 15 seconds. Advantages of this method were the relatively weak acid solutions used in the electrolyte bath, and short operating time.

One of the main uses for electropolishing tungsten wire is for specimens in the field-ion microscope.[29] The specimen tips have radii of 100-200 $\mathring{A}$ and shank angles of 10-30°; ideally they should have a smooth surface and be free of contamination and etch marks. The tip is usually prepared by an electropolishing technique where a wire is dipped through a thin layer of electrolyte floating on an inert liquid such as carbon tetrachloride. A potential is applied between the wire

and a second electrode and polishing is continued until the lower part of the wire drops off. Often the polishing is resumed for a few seconds at a slightly lower voltage to remove deformed material from the fracture region (backpolishing). This method has also been extensively used to prepare individual tungsten wire specimens for field-emission microscopy.

Little scientific background can be given for the mostly empirical art of producing fine emitter tips. Electrolytic polishing processes other than those mentioned previously include molten sodium nitrate in which the wire is dipped into the melt, and a potential of 0 or 0.5 to 1 V ac is applied and aqueous solutions of sodium hydroxide with applied potentials of 1 to 5 V ac.[31]

CHAPTER III

PROCEDURE

The experimental procedures used to chemically expose the W fibers above the surface of the matrix, shape (point) the tips of the tungsten fibers, and to selectively dissolve the W fibers from the matrix were similar and are described together. A brief description of the electrolytic etching procedures and associated problems is also presented.

Materials used in this investigation were UO_2 from Nuclear Materials and Equipment Corporation and W from Fairmont Chemical Company, formed into the composite structures by unidirectional solidification. For chemical etching of these UO_2-W composites, the samples were first mechanically polished to a bright finish using successively finer SiC grinding paper (180, 320, 600 grit) and finishing with one micron diamond paste on a nylon cloth. Reflected light examination was used to check the surface prior to chemical etching. A standard etching solution after Manley[8] was prepared as in Table 1. This starting etch was modified to determine the effects of the etch on the UO_2 matrix, on the W pins, and the mutual attack; it was also used as a basis for shaping the tips of the W pins. Polished samples usually in the shape of wafers were clipped to a shaft rotating at about 20 rpm and immersed in this etching solution for a predetermined amount of time, then rinsed by

Table 1. Composition of Standard Etch Solution

20 ml saturated chromic acid
10 ml glacial acetic acid
7 ml concentrated nitric acid
5 ml 48 percent hydrofluoric acid

rotation in a water bath and ultrasonically cleaned in water. Figure 1 shows the apparatus used for this procedure.

The effects of etching time from one to sixty minutes and rotation speeds up to 60 rpm were studied along with intentional variations in the composition of the etch.

Initially, it was thought that chemical and electrolytic etching techniques used to shape emitter tips for the field ion microscope could be used to thin the metal pins of the composite. Techniques which were applied to the UO_2-W composites included electropolishing in molten salt baths, in electrolyte solutions, and in double-layer solutions of an electrolyte and a non-conducting liquid. Insulation of the metallic support proved to be the main problem in this area; pin coatings tried were fingernail polish, Cervaseal UHV Bakable Leak Sealant, and paraffin.

Selective dissolution of the W pins without damage to the UO_2 matrix was studied through the use of chemical etchants; combinations of acids, alkalis, and oxidants were investigated.

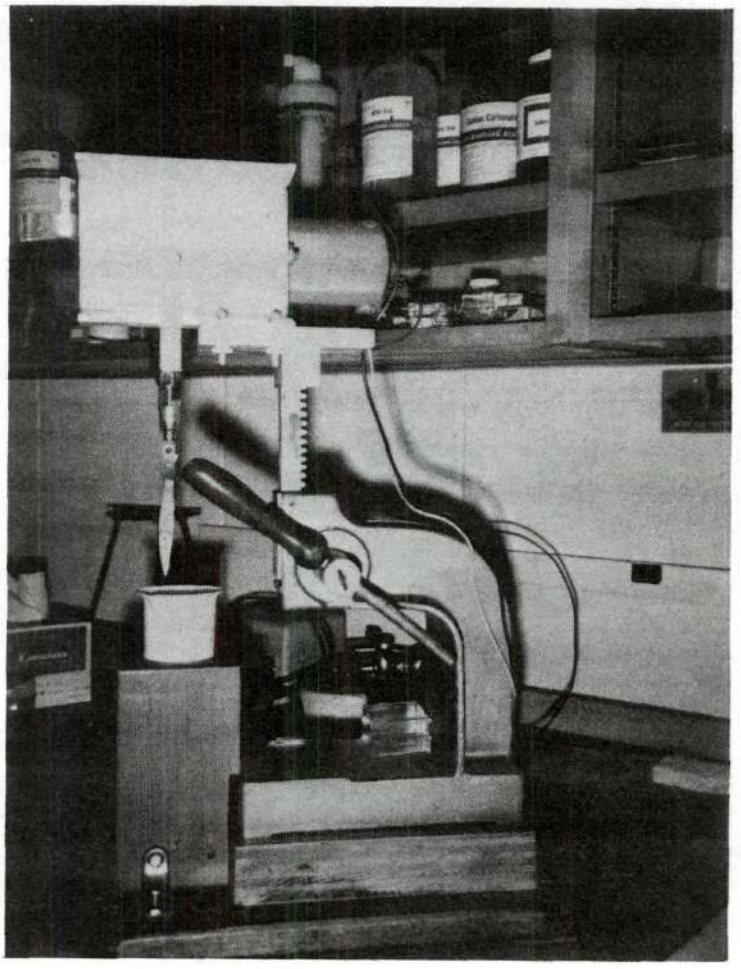

Figure 1. Apparatus Used for Etching UO_2-W Samples.

CHAPTER IV

RESULTS AND DISCUSSION

Three areas of chemical and electrolytic etching of UO_2-W composites to form structures suitable for field electron emission were studied: investigation of various etching techniques to selectively remove the UO_2 matrix without attack on the W fibers; shaping of the W fibers by chemical or electrolytic methods or a combination of both, either as a separate process or as part of the initial etching procedure; selective removal of the W fibers, leaving the UO_2 matrix unaffected. The results of various etching procedures to achieve these different structures are presented and discussed.

Etching to Expose the W Pins

Selective etching of the UO_2-W composites to expose the W pins by removal of the UO_2 matrix through the use of various chemical etchants is discussed in this section. Studies conducted within this area include the effect of etching time on exposed fiber heights, the influence of sample rotation speeds on etching characteristics and the general effect of variations in etch solution composition on the etching process. The study of fiber heights as a function of etching times showed a linear relationship to be present. Variation of rotation speeds resulted in changes in matrix topography. The composition of the etchant has a very pronounced effect on the pin configuration; it was found that even minute changes produced marked

results.

The effects of etching time upon fiber length were initially studied using the standard etching solution, shown in Table 1. A UO_2-W sample was etched for successive periods of 20, 40, and 60 minutes; the exposed lengths were 2.98, 5.61, and 8.24 microns, respectively. These lengths were determined from scanning electron micrographs using the following formula:

$$F = \frac{P}{\cos \alpha \, M} \tag{13}$$

where:

F = actual fiber length

P = projected fiber length as measured from SEM micrograph

cos α = tilt angle (SEM viewing angle)

M = magnification

Results of these measurements are shown in Figure 2.

The effect of rotation speed on the etching behavior of UO_2-W samples was also studied. Samples were rotated at speeds of 20, 30, and 60 rpm in the standard etch solution for exposure times of 20, 30, and 40 minutes. At 20 rpm (see Figure 3) the W fibers were clearly exposed and standing erect. Figure 4 shows a sample etched at 30 rpm; there is a "dune" effect in which the matrix is higher on one side of the pin than on the other. This was probably due to the etchant being swept past the fibers too fast for equal attack. The fibers interrupted the liquid flow, and the areas directly behind the fibers were not uniformly exposed to the etchant. At 60 rpm, Figure 5,

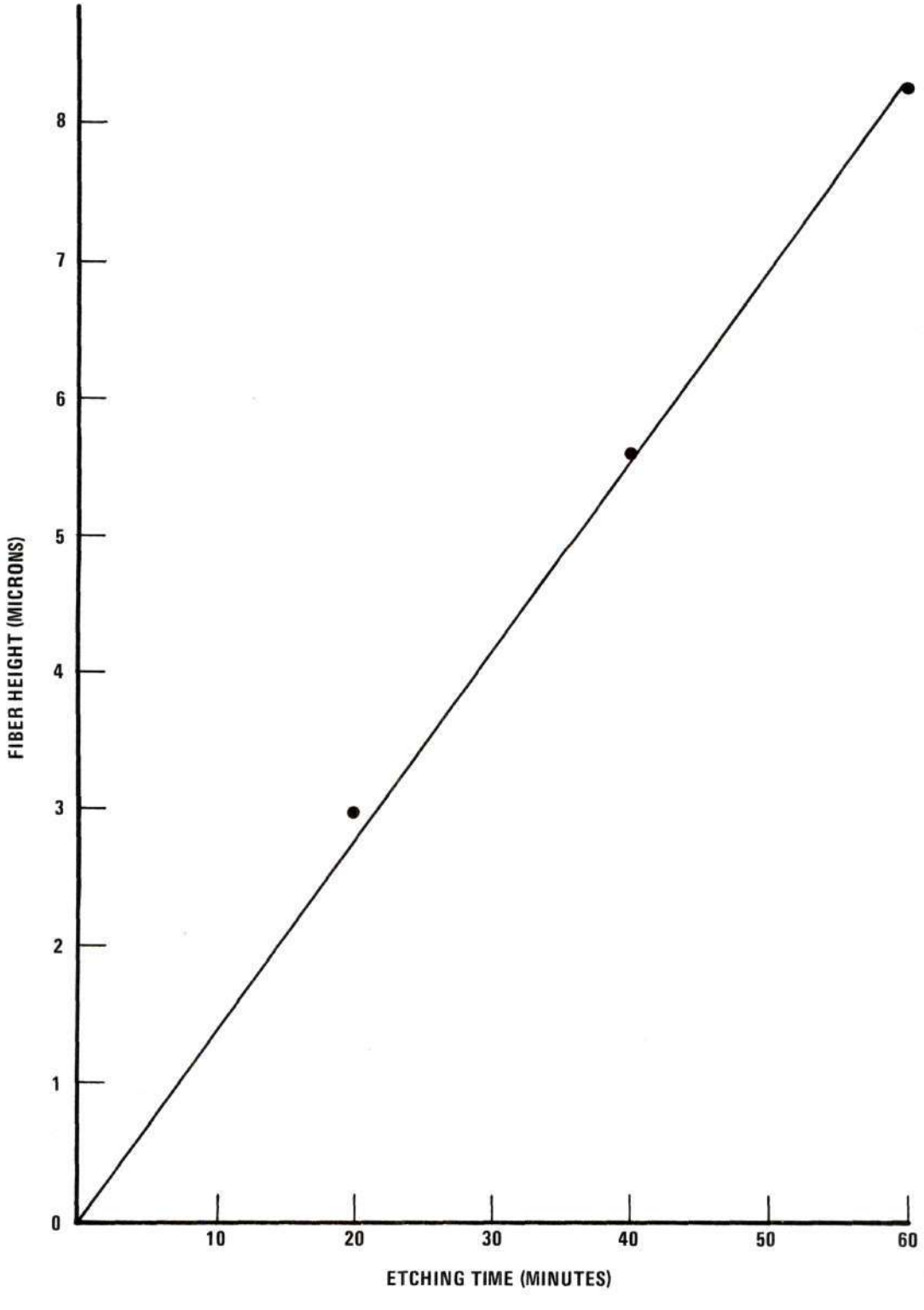

Figure 2. Etching Time Versus Exposed Fiber Heights for Chemically Etched UO_2-W Sample Using Standard Etch Solution.

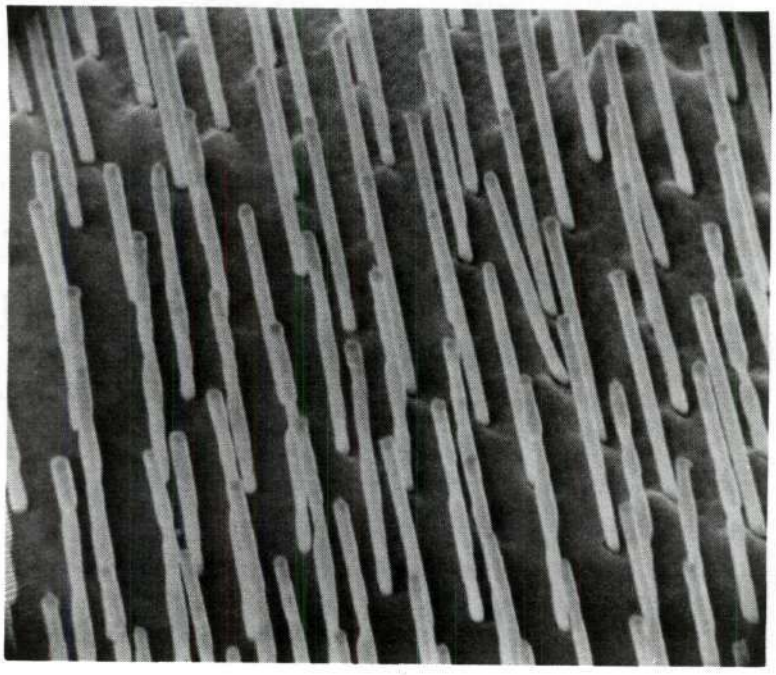

Figure 3. UO_2-W Sample Rotated at 20 rpm in Standard Etch for 20 Minutes. 5400 X.

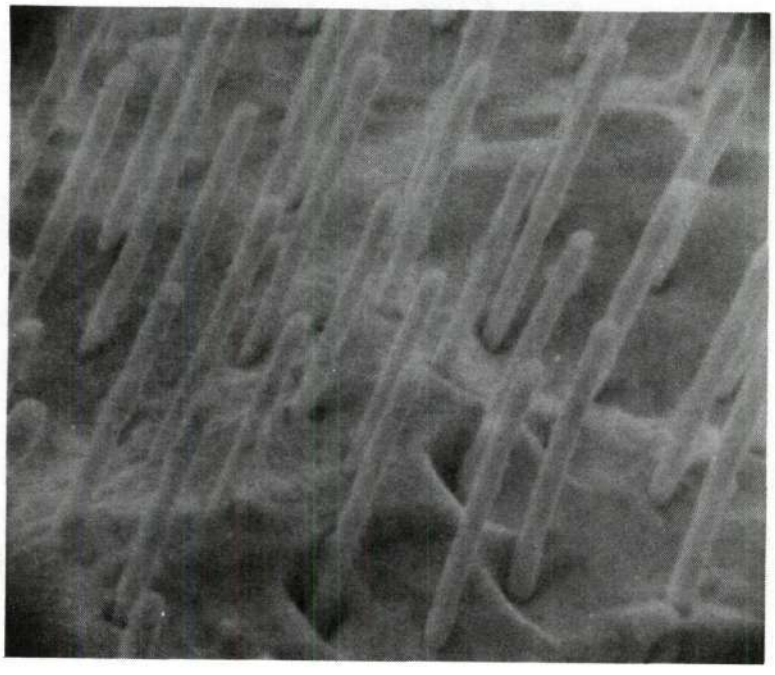

Figure 4. UO_2-W Sample Rotated at 30 rpm in Standard Etch for 30 Minutes. 5250 X.

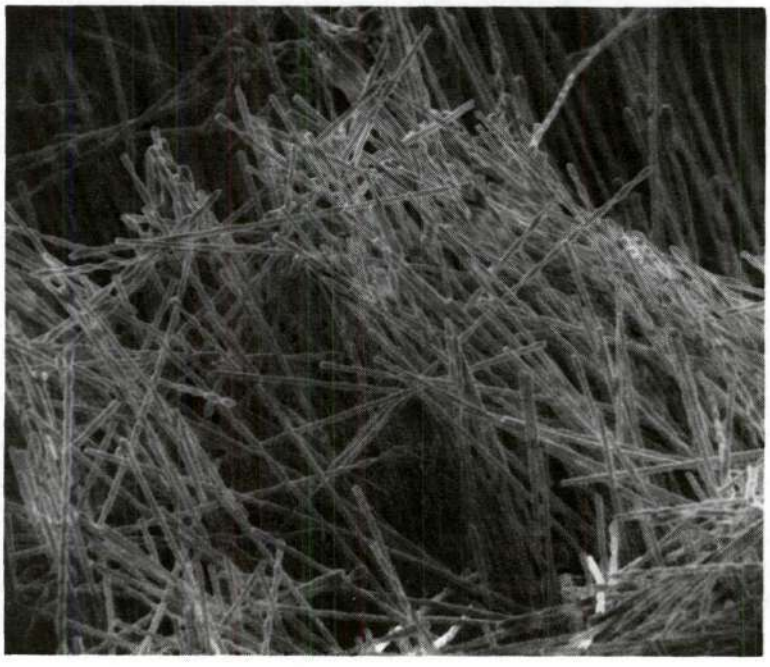

Figure 5. UO_2-W Sample Rotated at 60 rpm in Standard Etch for 40 Minutes. 2170 X.

the fibers were bunched together at the tips, and many were pushed over. Apparently at the fast rotation speed the long fibers were buffeted around and bent. As a result of these studies, 20 rpm was used as the standard rotation speed.

In an attempt to produce longer fibers with less chemical attack on the fibers, an etchant using lower HF concentration was used. The hydrofluoric acid was reduced from 5 ml to 2 ml; the remaining constituents of the etch were unchanged. Using an etching solution containing the lower concentration of HF, a study of etching time versus fiber height was made to determine the possible effect of HF on the tungsten fibers. Fiber heights ranged from 3.9 to 15.9 μm, as shown by curves A and B in Figure 6. Samples were immersed for 10, 20, and 30 minutes at rotation speeds of approximately 20 rpm and bath temperatures of approximately 40°C.

Results were erratic and difficult to reproduce; occasionally fibers up to 40 μm were produced. As a rule, these fibers were well shaped and showed no evidence of attack when etched up to 20 minutes, as shown in Figure 7. This indicated that in previous etching studies the etch was attacking the metal as well as the oxide. The tungsten was dissolved at a slower rate than the UO_2, resulting in short, pointed fibers. An etchant made by the standard etch minus HF was used to determine the effect of HF in the etching reactions. The sample was immersed for 40 minutes at 60 rpm in a 42°C etch bath. No attack occurred on either the fibers or the matrix, indicating HF to be a necessary component for etching.

One disadvantage of using an etchant containing lower concentrations

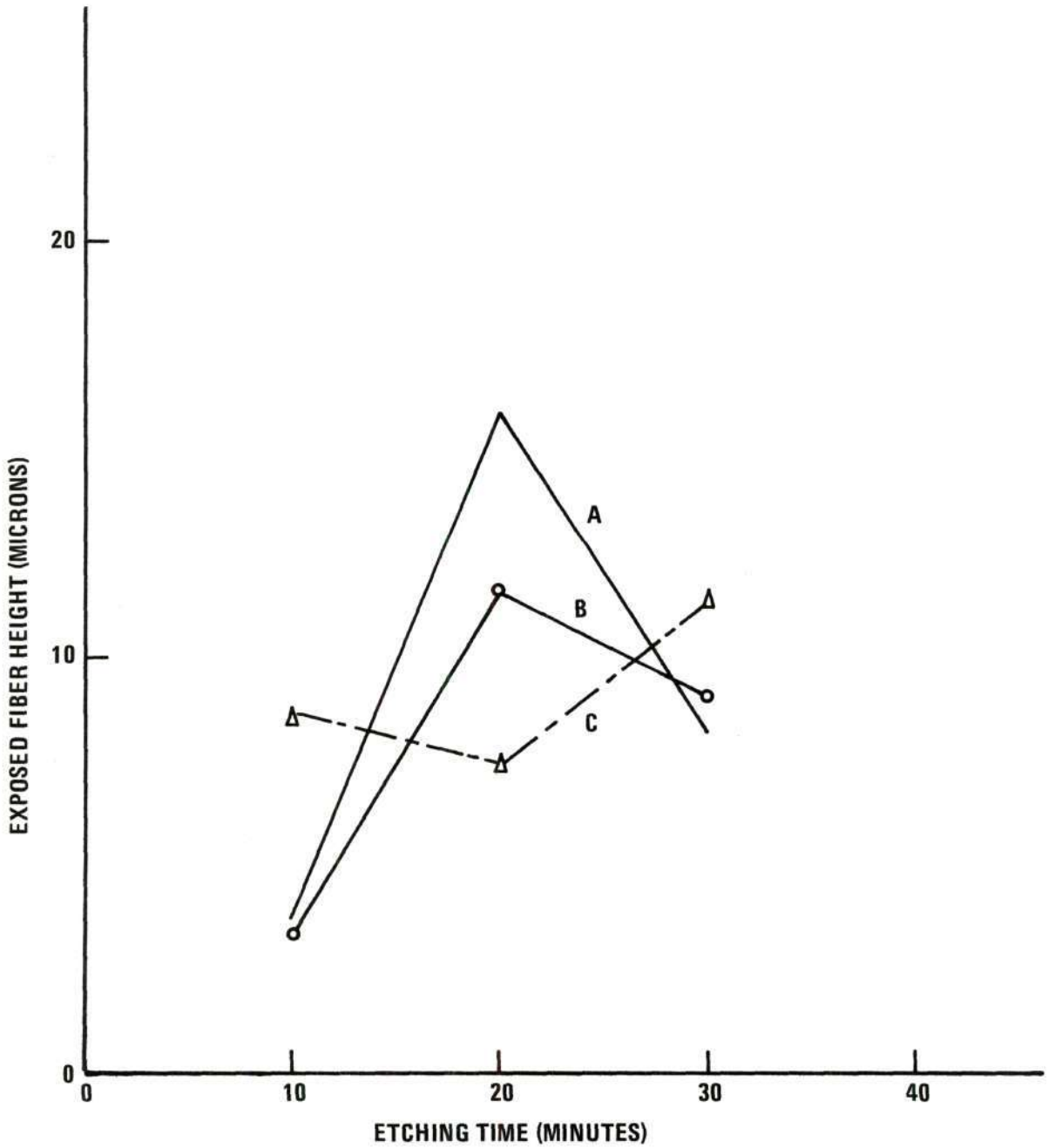

Figure 6. Exposed Fiber Height Versus Etching Time Using Decreased HF: HNO_3 Ratio in Standard Etch Solution. (Solid Lines, A & B, Indicate Etch Solution Containing Lower HF Concentration--2 ml) (Broken Line, C, Indicates Etch Solution Containing Lower HF and Lower HNO_3 Concentrations--2 ml HF and 3 ml HNO_3)

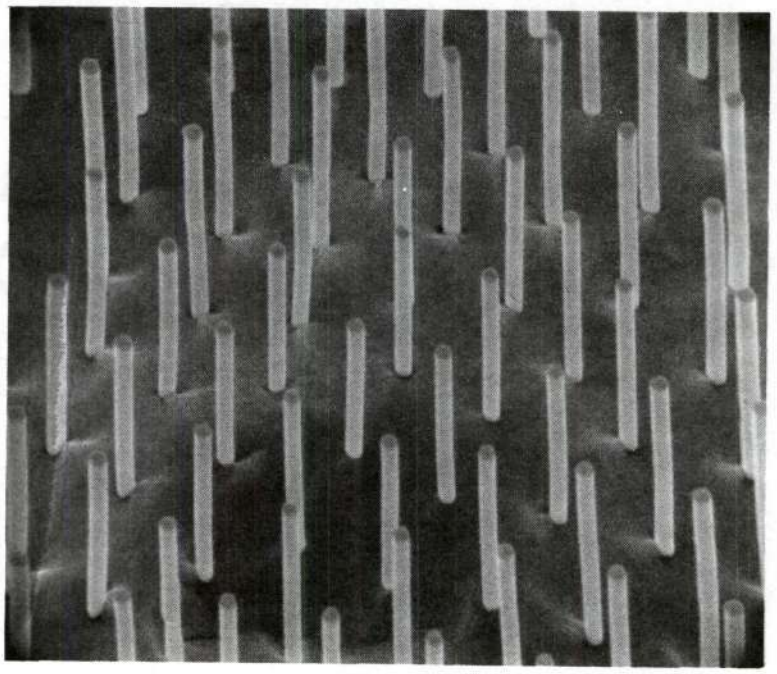

Figure 7. Sample Etched for 10 Minutes in Standard Etch Solution Containing 2 ml HF. 5300 X.

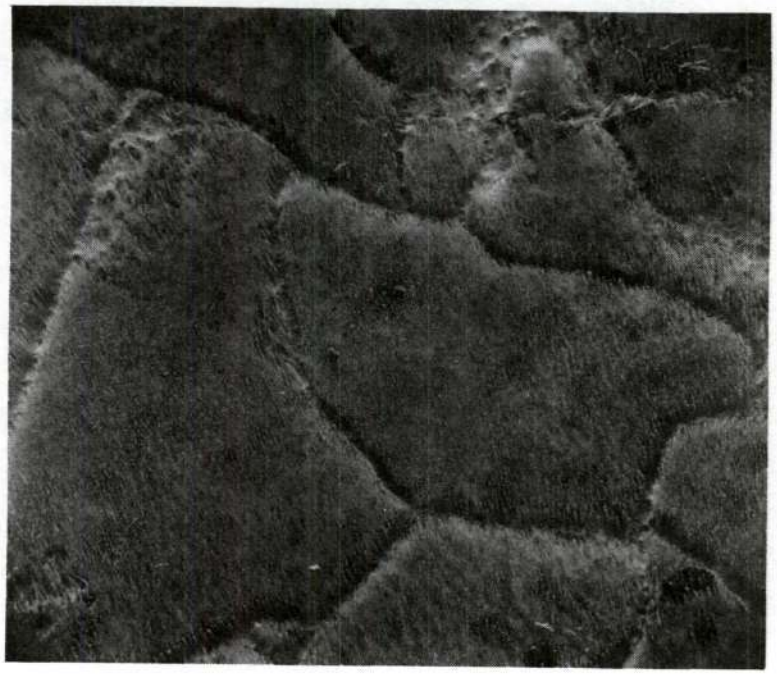

Figure 8. UO_2-W Sample Etched in Standard Etch Solution Containing 2 ml HF and 3 ml HNO_3. 130 X.

of HF is an increased UO_2 grain boundary attack by the increased concentration of HNO_3. An attempt to reduce this attack was made by decreasing the concentration of HNO_3 from 7 ml to 3 ml in a low HF etching solution. Several samples were etched in this solution (Figure 8) using rotation speeds of approximately 20 rpm and 40°C bath temperature. Figure 6 is a result of a study of etching time versus fiber height made to determine the effect of decreased HF:HNO_3 concentrations on length of the tungsten fibers. The results obtained indicated an increase in fiber height with etching time up to 20 minutes. After 20 minutes, there was a decrease in fiber length, possibly due to the fibers being attacked by the acid etching solution. This indicated a maximum etching time for greatest length to be about 20 minutes.

In the etching solution containing low concentrations of both HF and HNO_3 a general trend toward increased length with increased exposure time was noted in Figure 6, shown by curve C. However, a slight decrease in fiber length was seen between 10 and 20 minutes exposure time. This was probably due to sample variations in both growth modes and preliminary preparation.

Figure 9 shows both long and short fibers. Apparently, due to a growth phenomenon of some sort, certain areas within the oxide matrix were more rapidly attacked than others. This increased attack may be due to orientation of the cells or a stress concentration within the cells. When exposed to the acid etching solution, these areas of higher energy were preferentially attacked as were the grain boundaries. In this figure, the short fibers are erect and well formed while the

Figure 9. UO_2-W Sample Containing Both Long and Short Fibers.

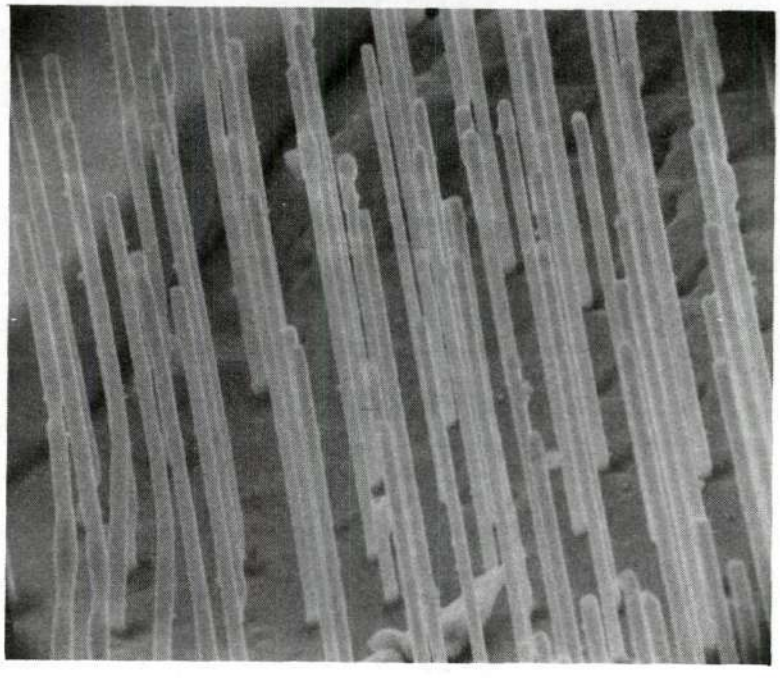

Figure 10. W Fibers Produced By Etching UO_2-W Composite in Standard Etch Solution Containing 2 ml HF. 5600 X.

long fibers are bunched together and slightly twisted. The short fibers are approximately 12 μm long, while the long fibers are of an unknown length. This behavior was not common in the samples.

Shaping the Fibers

Chemical and electrolytic etching techniques similar to those used to produce emitters for the field ion microscope were tested as techniques to shape the W fibers in composite samples which had been initially etched to expose the W fibers above the UO_2 matrix. These techniques included molten salt baths and electropolishing in double-layer solutions of an electrolyte and a non-electrolyte and chemical etchants. The most favorable results, however, were produced by modification of the standard etch solution.

The long, well shaped fibers produced by etching in the lower HF solution (Figure 10) seemed particularly well suited to electrochemical methods of shaping fibers. Solutions used, electrical requirements, and exposure times are summarized in Table 2. Insulation of the metallic support pin proved to be the main problem. The samples were mounted on SEM pins with silver paste; these pins must be insulated from the electrolyte to force current to flow through the sample. Insulating coatings tried were fingernail polish, Cervaseal UHV Bakable Leak Sealant, and paraffin. Of these, paraffin worked best but was difficult to apply.

Of the electrolytes shown in Table 2, only the Na_2CO_3 solutions showed promise. Long pointed fibers were formed but attack on the sides of the fibers was noted, resulting in a faceted effect as shown

Table 2. Electrochemical Methods Used to Shape Fibers

Electrolyte Bath	Electrical Requirement	Time
fused $NaNO_2$	None	5 min.
5 wt% NaOH in NaOH-CCl_4 double-layer bath	5-15V ac; 250-300 ma	1-5 min.
1 wt% Na_2CO_3	10V ac; 40 ma	2 min.
5 wt% Na_2CO_3	20V ac; 75 ma	5 min.
10 wt% NaOH	7.2V-9.8V ac	2-12 min.

in Figure 11.

The alkali hydroxide and nitrate solutions produced severe attack on both fibers and matrix. The double-layer solutions were very difficult to utilize in small samples (maximum fiber length of 40 μ) and again, insulation was a problem.

During routine etching of UO_2-W composites to expose the W fibers using the standard chromic acid etch, it was noted that random fibers and occasionally large areas of fibers became pointed after about 30 minutes of treatment. Intentional variations of the composition of the standard etch were made to assess its influence on the shape of the W fiber tips. A slight increase in the HF concentration (from 5 to 6 ml) and an increase in etch temperature from 25°C to 40°C were used along with the standard etching procedure; etching time was 40 minutes and rotation speed 18 rpm. Samples treated in this manner were uniformly etched and the tips sharpened to a diameter 50 to 100 times less than that of the fiber diameter. Figure 12 shows a typical UO_2-W composite after etching with the solution containing the higher concentration of HF at 40°C. These fibers are approximately 4 μ long; the increased attack on the W fibers was believed to be due to the increased $HF:HNO_3$ ratio and the higher etchant temperature.

Removing Tungsten Fibers

Techniques to selectively dissolve the W fibers without affecting the UO_2 matrix were also studied. Methods used included hot acids, molten hydroxide baths, and combinations of oxidants and alkalies. The hot acids and molten hydroxide baths severely attacked both the fibers

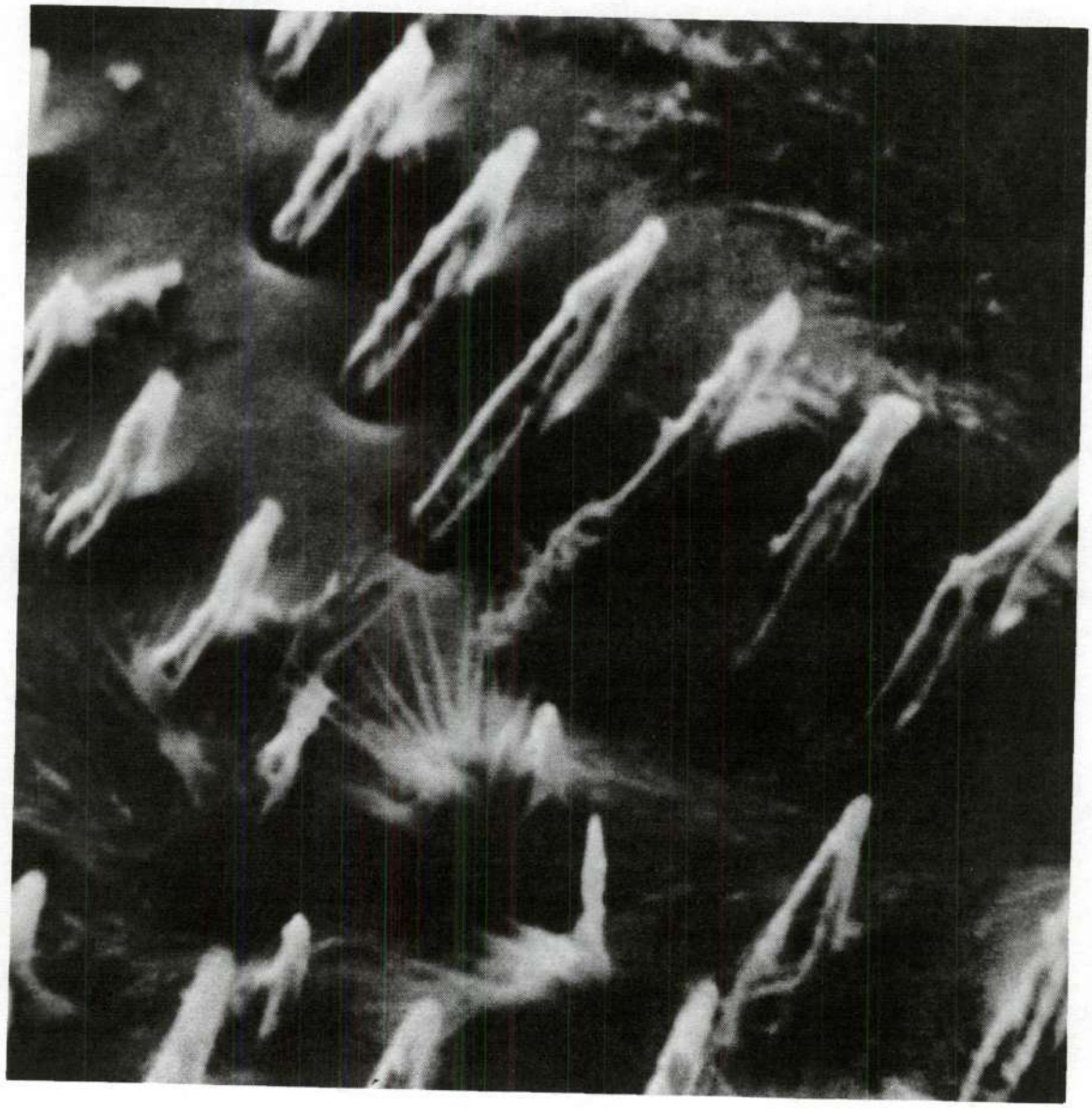

Figure 11. Electrochemical Shaping of UO_2-W Composites Using Five Percent Na_2CO_3. 12,200 X.

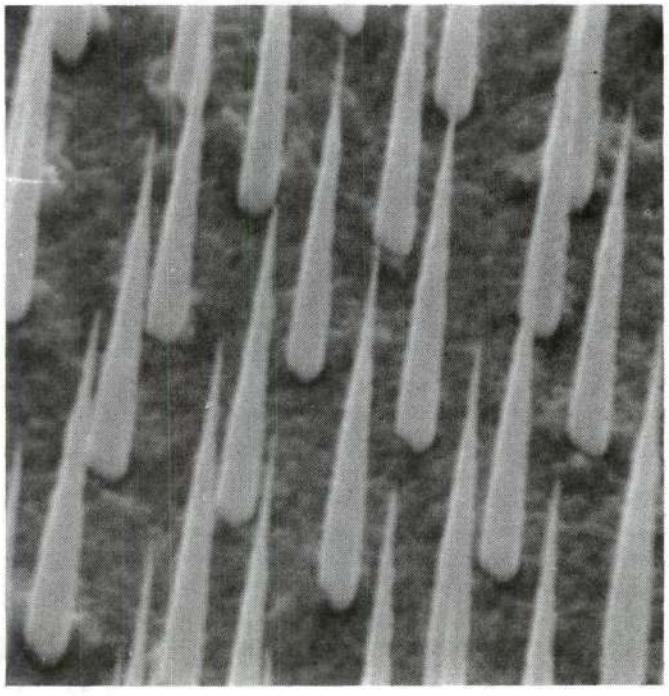

Figure 12. Chemical Shaping of UO_2-W Sample Using Increased Concentration of HF in Standard Etch Solution. 8500 X.

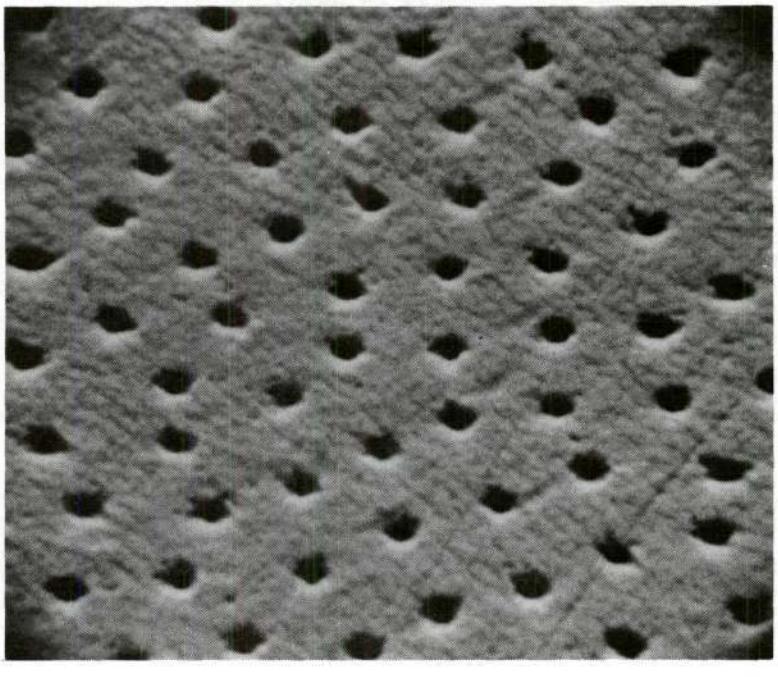

Figure 13. Removal of W Fibers Using $K_3Fe(CN)_6$ and NaOH Solution. 6300 X.

and the matrix. An etchant consisting of an oxidant and an alkali, resulted in very clean removal of the W fibers and little or no attack on the UO_2 matrix.

Samples used for the selective removal of W fibers were polished to a bright finish (as described in Procedure); no etching to remove the UO_2 matrix was used. Several chemical etchants were tried for the removal of W fibers.

The first etchant studied consisted of:

20 ml hot H_2O (64°C)

10 ml concentrated HNO_3

10 ml 48 percent HF

The sample was immersed for five minutes at a rotation speed of 20 rpm. This treatment resulted in a great deal of attack on both the fibers and the matrix.

Molten NaOH was also studied. The sample was dipped into the hydroxide bath for four seconds; handling of the sample in this process proved to be difficult. SEM micrographs showed a great deal of attack on both fibers and matrix, similar to that observed after the acid treatment in the first etchant.

An etchant for tungsten consisting of an oxidant and an alkali was tried next. The solution was composed of a 1:1 volume ratio of 30 percent $K_3Fe(CN)_6$ and 10 percent NaOH. The etching procedure consisted of rotating the UO_2-W sample in the etchant solution (35°C) at 20 rpm for 15 minutes. SEM analysis, Figure 13, showed many uniformly spaced holes in the place of W fibers.

An attempt was made to determine the depth of these holes by

measurement of the sample thickness before and after polishing away the matrix to a flat surface. This method has many disadvantages: non-parallelism of sides, insensitivity of thickness and difficulty in determining exact hole depth. As a result of these disadvantages, no accurate hole depth information was obtained.

CHAPTER V

CONCLUSIONS

UO_2-W composites may be etched easily using an etchant consisting of 20 ml saturated chromic acid, 10 ml glacial acetic acid, 7 ml concentrated nitric acid, and 5 ml 48 percent hydrofluoric acid. Exposure of the composite to this stirred acid mixture results in the removal of the UO_2 matrix and exposure of the W fibers. Heights of these fibers vary linearly with etch exposure time and may range up to 40 μm in length.

Sample rotation speeds influence the shape of the fibers and the topography of the matrix. Best results are obtained when a rotation speed of about 20 rpm is used; at faster speeds the fibers are bent and broken and the matrix uneven.

Reduction in the HF concentration from 5 ml to 2 ml produces longer W fibers with less chemical attack. To prevent increased grain boundary attack, the HNO_3 concentration must also be reduced from 7 ml to 3 ml.

Fiber length also varies with exposure time in the etchants containing lower HF concentrations and lower HF and HNO_3 concentrations. Exposure times up to 20 minutes in the solution containing lower HF produce a linear increase in fiber length, while a general trend toward longer fibers at all exposure times is noted in the etchant containing both lower HF and HNO_3.

Shaping of the W fibers for the desired emitter pin geometry is best done by an increase in the HF concentration from 5 ml to 6 ml in the standard etch solution, although promising results are obtained using electrolysis of the sample in Na_2CO_3 solutions.

Removal of the W fibers from the composite structure by the use of a 1:1 volume solution of 30 percent $K_3Fe(CN)_6$ and 10 percent NaOH results in many well shaped holes where the W pins had been with little or no damage to the UO_2 matrix. No accurate hole depth information was obtained due to inadequate methods of measurement.

CHAPTER VI

RECOMMENDATIONS

Chemical etchants other than the chromic acid-based etch used in this investigation should be tested. Also, variations in the relative amounts of chromic acid, and acetic acid should be studied for their effects on both the UO_2 of the matrix and the W fibers.

The study of the effect of decreased HF and HNO_3 concentrations on exposed fiber lengths and the variations in etching times should be investigated more closely to determine the possibility of a linear relationship between the fiber height and etching time.

Methods of shaping the fibers for the desired pin geometry should include those which produce less attack on the fibers, allowing fibers to be long and pointed. Electrolysis of Na_2CO_3 solutions shows promise; perhaps lower voltages and concentrations than those used in this report would produce satisfactory results.

Future work in the area of removal of the W fibers without damage to the matrix might include other combinations of oxidants and alkalies. Also, methods for determining hole depth need to be found. Improvements might consist of a jig to insure parallelity of the sample faces during polishing and a very sensitive method of measuring changes in sample thickness. Perhaps replication or resistivity measurements would be an alternative method of measuring hole depth.

BIBLIOGRAPHY

1. A. T. Chapman, G. W. Clark, and D. E. Hendrix, "UO_2-W Cermets Produced by Unidirectional Solidification," 53 (1), 60-61 (1970).

2. M. D. Watson, D. N. Hill, and A. T. Chapman, "Solidification Behavior of Stabilized ZrO_2-W," Journal American Ceramics Soc. 53(2), 112-113 (1970).

3. "Melt-Grown Oxide-Metal Composites," Final Technical Report No. 2, Advanced Projects Research Agency, Department of Defense, ARPA Order No. 1637, Contract No. DAAHOI-70-C-1157.

4. H. E. Cline, "Multineedle Field Emission from the Ni-W Eutectic," Journal Applied Physics, 41 (1), 76-81 (1970).

5. W. Desorbo and H. E. Cline, "Metal Membranes with Uniform Submicron-Size Pores," Journal Applied Physics, 41 (4), 2099-2105, (1970).

6. R. J. Gerdes, A. T. Chapman, and G. W. Clark, "Refractory Oxide-Metal Composites: Scanning Electron Microscopy and X-ray Diffraction of Uranium Dioxide-Tungsten," Science, 167 (2), 979-980 (1970).

7. J. Belle, Uranium Dioxide: Properties and Nuclear Applications, Washington, Naval Reactors, Div. of Reactor Development, U. S. Atomic Energy Commission, 1961, 726 pp.

8. A. Bassi, "A Metallographic Technique for Uranium Dioxide," Energia Nuclare, 8 (8), 537-538 (1961).

9. A. Bassi and G. Camona, "A Chemical Polishing for Uranium Dioxide," Energia Nuclare, 10 (5), 277-279 (1963).

10. A. J. Manley, "The Thinning of Sintered Uranium Dioxide to Electron Transparency by Chemical Polishing," Journal Nuclear Materials, 15 (1), 143-145 (1965).

11. M. P. Bauleke, "Chemical Thinning of Pneumatically Impacted UO_2 for Electron Transmission Microscopy," U. S. Atomic Energy Commission (BNML-416), 11 pp.

12. A. Briggs, "Dislocation Etching and Chemical Polishing Studies on UO_2 Single Crystals," Transaction of British Ceramic Society, 60 (6), 505-516 (1961).

13. E. A. Kanevskii, A. P. Filippov, and N. V. Timofeeva, "Composition of Gases Produced by the Interaction of UO_2 with HNO_3," Atomic Energy (USSR), 13 (4), 484-486 (1962).

14. A. P. Filippov, E. A. Kanevskii, and N. V. Timofeeva, "Reaction of UO_2 with HNO_2 in Solutions of H_2SO_4," Zh. Prikl. Khim., 38 (3), 658-660 (1965).

15. F. Habashi and G. A. Thurston, "Kinetics and Mechanism of the Dissolution of UO_2", Energy Nuclear, 14 (4), 238-244 (1967).

16. G. D. Rieck, Tungsten and Its Compounds, Pergamon Press, Oxford, 1967, p. 41.

17. J. Neugebauer and A. Kiss, "Reactions of Tungsten, Molybdenum, and Their Oxides in the System $K_3Fe(CN)_6$-OH-H_2O. I. Dissolution Rate of Tungsten," Acta. Chem. Acad. Sci. Hung., 44(3), 241-251 (1965).

18. T. Milner, "Ammoniacal Cupric Hydroxide as a Solvent for Tungsten," Z. Anorg. Allgem, Chem. 212 (4), 284-288 (1933).

19. S. I. Geesev and U. I. Kumov, "Study of the Reactions Between Tungsten and Oxalic Acid-Hydrogen Peroxide Mixtures," Zhur. Anal. Khim. 3 (1), 373-376 (1948).

20. D. Robbins, "The Dissolution of Tungsten in Mixtures of Hydrofluoric and Nitric Acids," Metallurgia, 55 (7), 257 (1957).

21. G. D. Barnett and A. Miller, "Chemical Etching of Tungsten," U. S. Patent #3,232,803, Feb. 1, 1966, Appl. April 16, 1963.

22. M. J. Sienko and R. A. Plane, Chemistry, McGraw-Hill, Inc., New York (1961) p. 278.

23. J. G. Davis, "Electrochemical Polishing and Etching of Tungsten," Journal of Scientific Instruments, 35 (6), 149 (1958).

24. E. Farshauer, "Electrolytic Polishing of Tungsten and Molybdenum," German Patent # 974,610 (Cl. 48a) Appl. Dec. 17, 1943.

25. Y. A. Leizgol'd, "Electrolyte for the Electrochemical Polishing of Tungsten," USSR Patent # 210,598 (Cl. C 23b) Appl. Mar. 25, 1967.

26. "Manufacture of Thin Structures by Electrolytic Etching," Britain Patent # 1,009,518 (Cl. C 23b) Nov. 10, 1965. Appl. July 6, 1962.

27. H. P. Weinberg, "Method of Etching Refractory Metal Based Materials Uniformly Along a Surface," U. S. Patent # 3,411,999. Appl. Dec. 10, 1965. Nov. 19, 1968.

28. A. A. Lataweic and G. H. Lockwood, "Method of Electropolishing Tungsten Wire," U. S. Patent # 3,287,238. Appl. June 7, 1963. Nov. 22, 1966.

29. J. E. Fosth, B. Loberg, and H. Norden, "Preparation of Contamination Free Tungsten Specimens for the Field Ion Microscope," Journal of Scientific Instruments, 44 (11), 1044-1045 (1967).

30. H. R. Cortes, "Electropolishing Refractory Metals," U. S. Patent # 3,033,769. Appl. Dec. 23, 1959. May 8, 1962.

31. E. W. Muller, Field Ionization and Field Ion Microscope, McGraw-Hill, Inc., New York, 1968, p. 128-129.